ISSN 1063-7834, Physics of the Solid State, 2013, Vol. 55, No. 1, pp. 140–144. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © Yu.V. Knyazev, N.I. Kourov, A.V. Lukoyanov, Yu.I. Kuz'min, 2013, published in Fizika Tverdogo Tela, 2013, Vol. 55, No. 1, pp. 125–129.

OPTICAL PROPERTIES

Optical Spectroscopy and Electronic Structure of the $GdCu_x$ Compounds ($x = 1, 2, 5$)

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Received May 4, 2012

Abstract—Optical properties of the GdCu, $GdCu_2$, and $GdCu_5$ compounds with various crystal lattices have been investigated using ellipsometry in a spectral range of 0.22–16 μm. Theoretical calculations of the electronic structure of these intermetallic compounds have been performed in the approximation of local electron density with the correction for strong electron correlations in a 4*f* shell of gadolinium ions. Based on the results of calculations, the interpretation of experimental spectra of interband optical conductivity has been proposed. The plasma and relaxation frequencies of conduction electrons have been determined.

DOI: 10.1134/S1063783413010204

1. INTRODUCTION

Ordered phases (GdCu, $GdCu_2$, and $GdCu_5$) with various crystal lattices and diverse magnetic and electrical properties, which are of interest for investigation, are formed in binary alloys of the Gd–Cu system. The GdCu intermetallic compound can be ordered in a face-centered lattice of the CsCl type or in the orthorhombic lattice of the FeB type depending on thermal treatment conditions [1], while $GdCu_2$ and $GdCu_5$ possess the orthorhombic [2] and hexagonal (of the $CaCu_5$ type) [3] structures, respectively. At temperatures below the Néel point T_N, these alloys acquire the collinear antiferromagnetic ordering, for which magnetic moments are determined almost completely by Gd atoms. According to [4], the Néel points in these systems have the following values: $T_N =$ 142 K (GdCu), 48 K ($GdCu_2$), and 10 K ($GdCu_5$). Some investigations indicate the direct influence of specific features of electronic spectrum $E(\mathbf{k})$ of these intermetallic compounds on their magnetic and structural parameters. For example, according to [5], stabilization of the cubic structure of the CsCl type and the antiferromagnetic state in GdCu is provided by a low density of electronic states at the Fermi level E_F. Anomalies are observed in kinetic properties of mentioned systems, which are also attributed to the character of the distribution of the electron density near E_F and scattering features of conduction electrons [2, 6–8]. However, the approach to interpretation of physical characteristics of intermetallic compounds of the $GdCu_x$ family from the viewpoint of investigating the parameters of the band structure still has not acquired the proper development. Up to now, the calculation of the electronic structure by the LMTO method is implemented for the GdCu compound only [8, 9].

It is known that the reliable data on the features of $E(\mathbf{k})$ for metals and alloys can be obtained from spectroscopic measurements. In this context, we should mention studies [9–12], in which the features of localization of Cu 3*d* and Gd 4*f* states in the occupied part of the valence band of $GdCu_x$ ($x = 1, 2, 5$) compounds were studied by the X-ray and UV photoemission. It was established that as x increases, the width and location of 3*d* energy bands arranged closer to the Fermi level transform substantially (in contrast with a weak variation in parameters of 4*f* band). Optical investigations, in which the features of the structure of energy bands are reflected in dispersion curves of measured spectral characteristics, promote acquiring better understanding of the band structure of these compounds.

In this study, we performed a complex experimental-and-theoretical investigation of spectral and electronic characteristics of the GdCu, $GdCu_2$, and $GdCu_5$ compounds. The results of optical investigations in a wide wavelength region are presented. The theoretical interpretation of the obtained experimental data is performed based on band calculations of the electronic structure of these systems.

2. ELECTRONIC STRUCTURE

Self-consistent calculations of the electronic structure for Gd–Cu compounds were performed in the local spin density approximation allowing for strong

electron–electron interactions between electrons of 4*f* shell of Gd (the LSDA + *U* method [13]). Calculations were performed using the TB-LMTO ASA program package [14] based on the method of linearized muffin-tin orbitals in the approximation of atomic spheres. For all these compounds, we used a grid of *k* points in the reciprocal space with the total number of the points $12 \times 12 \times 12 = 1728$. The following electron configuration was considered for gadolinium ions: 6*s*, 6*p*, 5*d*, and 4*f*; and 4*s*, 4*p*, and 3*d* for copper ions. The atomic radius of gadolinium is 3.7 au and that of copper atoms is 2.7 au. Parameters of the direct and exchange Coulomb interactions for 4*f* shell of Gd were $U = 6.7$ eV and $J = 0.7$ eV similarly to the $GdNi_5$ compound [15]. The GdCu compound was calculated in the structure of the CsCl type with a lattice constant of 3.502 Å. The $GdCu_2$ intermetallic compound, which crystallizes in the orthorhombic structure, contains two formula units per unit cell. Its lattice parameters are as follows: $a = 4.305$ Å, $b = 6.848$ Å, and $c = 7.306$ Å. The $GdCu_5$ possesses the hexagonal structure of the $CaCu_5$ type with one formula unit per unit cell. Its lattice parameters are $a = 5.018$ Å and $c = 4.117$ Å. The Gd ions occupy crystallographic site 1*a* while the Cu ions occupy sites 2*c* and 3*g*.

Figure 1 presents the total densities of electronic states $N(E)$ for the GdCu, $GdCu_2$, and $GdCu_5$ compounds calculated for all spin directions upward (↑) and downward (↓). In all $N(E)$ states, intense narrow peaks in the spin-up system at energies of ~8 eV below E_F are formed with filled $4f_\uparrow$ states of Gd. Intense structures, which correspond to free $4f_\downarrow$ states, are arranged in limits of 2.0–3.5 eV above E_F. Occupied 3*d* states of Cu form rather extended bands in considered compounds; their parameters are almost identical for two spin directions in all cases. The width of these bands, which are not subjected to exchange splitting, considerably increases as the copper content in the alloy increases; this is accompanied by the shift of localization of their center of gravity shifts towards the Fermi level. Partial densities of states for 5*d* electrons of Gd (shaded segments), which form the extended low-intense energy bands, are also shown in Fig. 1. In general, the view of densities of 4*f* and 5*d* states of Gd atoms depend weakly on the composition of the $GdCu_x$ alloy while the width and profile of 3*d* band of Cu are subjected to substantial variations. Magnetic moments of gadolinium and copper atoms found by LSDA calculations are presented in the table.

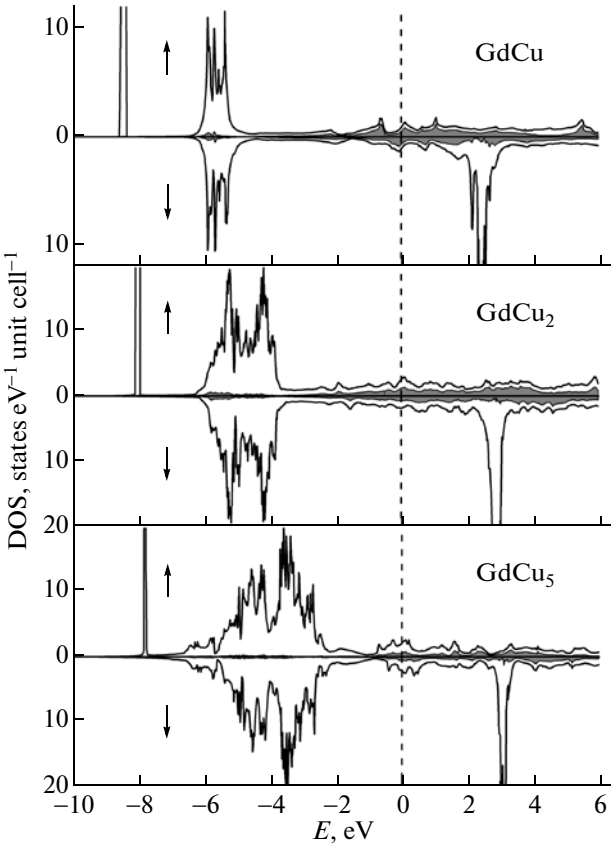

Fig. 1. Total density of electronic states of the GdCu, $GdCu_2$, and $GdCu_5$ compounds. Shaded segments represent the contribution of 5*d* states of gadolinium.

It should be noted that total electron densities of states found in LSDA calculations agree well with photoemission spectra of these compounds [9–12], which characterize their band structure at energies below E_F. The main features of experimental curves are present in calculated dependences $N(E)$: for all $GdCu_x$ compounds ($x = 1, 2, 5$), the occupied part of 4*f* band of Gd in $N(E)$ is localized near –8 eV. The tendency of the shift of the extended 3*d* band of Cu towards E_F with increasing *x* is reflected in the calculation. In addition, the calculated structure of the density of states of this band consisting of two broad max-

Magnetic moments of Gd and Cu ions, plasma and relaxation frequencies, and resistivity of intermetallic compounds GdCu, $GdCu_2$, and $GdCu_5$

Compound	M_{Gd}, μ_B	M_{Cu}, μ_B	$\gamma \times 10^{-14}$, s^{-1}	$\omega_p^2 \times 10^{-30}$, s^{-2}	ρ, $\mu\Omega$ cm
GdCu	7.19	0.02	0.9	31	41
$GdCu_2$	7.29	0.04	1.3	33	149
$GdCu_5$	7.34	0.06	1.1	34	71

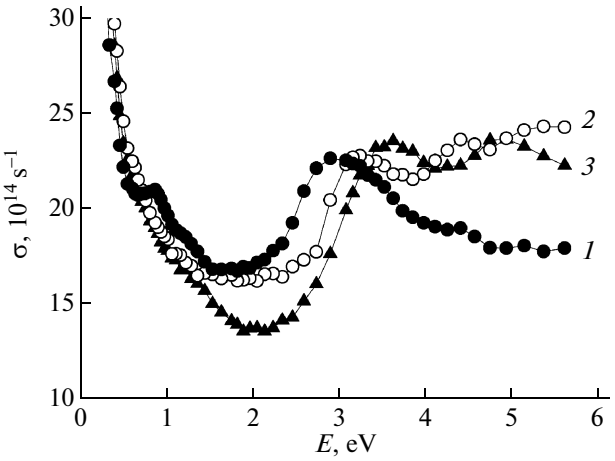

Fig. 2. Optical conductivity dispersion of (*1*) GdCu, (*2*) $GdCu_2$, and (*3*) $GdCu_5$ compounds.

ima for compounds with $x = 2$ and 5 and one maximum in the case $x = 1$ agrees with the experimental photoemission data.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Polycrystalline samples under study were melted in an arc furnace on a water-cooled copper tray in an argon atmosphere. Then they were homogenized at 1200 K for 6 h. Lattice parameters were determined by the X-ray structural analysis; they were close to the values found in [1, 3, 16].

Spectral properties of the GdCu, $GdCu_2$, and $GdCu_5$ compounds were investigated at room temperature in a wavelength region of 0.22–16 μm (0.078–5.640 eV). Optical constants, namely, refractive index $n(\omega)$ and absorption coefficient $k(\omega)$ (ω is the wave frequency of light) were measured by ellipsometry with a rotating analyzer for one and two (in the infrared region) reflections from the sample plane with an accuracy of 2–4%. Mirror sample surfaces of the 14th surface finish class were prepared by mechanical polishing on finely dispersed diamond pastes. Optical conductivity $\sigma(\omega) = nk\omega/2\pi$, being the most sensitive spectral parameter, which characterizes the frequency dependence and intensity of the optical response of the reflecting medium, was calculated by the values of $n(\omega)$ and $k(\omega)$.

Figure 2 shows the spectra of frequency dependences of optical conductivity of $GdCu_x$ compounds under study ($x = 1, 2, 5$). The behavior of $\sigma(E)$ in the low-energy region ($E \lesssim 1$ eV) is determined by an abrupt increase, which is typical of the Drude interaction mechanism of electrons with the electromagnetic wave ($\sigma \sim \omega^{-2}$). As the frequency of light increases, the character of dispersion of optical conductivity indicates the prevalent role of interband electron transitions. The appearance of a broad absorption band with

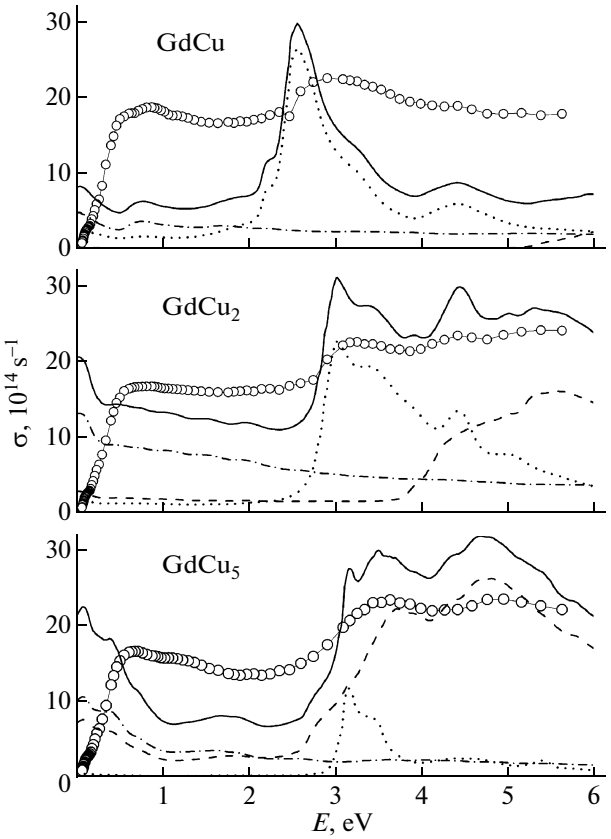

Fig. 3. Interband optical conductivity spectra for the GdCu, $GdCu_2$, and $GdCu_5$ compounds. Circles are the experimental data, and the solid line corresponds to the calculation (in arbitrary units). The dashed, dotted, and dash-and-dot lines correspond to partial contributions of the transitions Cu d–p, Gd f–d, and Gd d–p, respectively.

elements of a fine structure is observed for all compounds at $E > 2.5$ eV. The low-energy threshold of this band shifts towards higher frequencies as x of the alloy increases. A low-intense absorption maximum is found for the GdCu equiatomic alloy in a local energy region below 1 eV; it is absent for other compounds.

Distinctions, which are observed in dispersion dependences $\sigma(E)$ of compounds under study in the region of the quantum absorption of light are caused by modifying their band structure as the copper content varies. Therefore, it is of interest to compare the experimental interband optical conductivities $\sigma_{ib}(E)$ with these calculated from the electron densities of states (Fig. 1). Dependences $\sigma_{ib}(E)$ for all compounds are found by subtraction of intraband Drude contributions from experimental curves $\sigma(E)$ (Fig. 3). Interband optical conductivities, which were calculated by the corresponding dispersion dependences $N(E)$, are also presented in Fig. 3 in arbitrary units. In this case, the general pattern of the interband absorption, which manifests itself in optical properties, is a superposition of the structures from energy bands with oppositely directed spins. Model [17], according to which the

theoretical curve of optical conductivity $\sigma_{theor}(E)$ is represented in a form of the sum of all interband transitions for this compound, was used for the calculation. This approach was successfully used previously to calculate the spectral properties of a series of intermetallic compounds R_2Fe_{17} (R is the rare-earth metal) [18, 19].

All paired convolutions were summed according to the number of ions of various types in the unit cell. It turned out that interband transitions between f–d states of Gd ions and p–d states of Cu ions introduce the most essential contribution to the final value of $\sigma_{theor}(E)$. Transitions of $5d$–$4f$ types in the spin-down band system form a broad asymmetric band with an abrupt low-energy slope in the calculated optical conductivity for all compounds. In this case, $3d$–$4p$ transitions at copper ions in both spin systems introduce the contribution essential by conductivity only to $GdCu_2$ and $GdCu_5$ (above energies of 3.8 and 2.6 eV, respectively). It follows from Fig. 3 that the contribution from transitions between the p and d states of Gd ions is almost monotonic over the entire range under investigation excluding low-energy portion $E < 0.5$ eV.

The comparison shows that the superposition of all mentioned convolutions of densities of states in general reproduces the main features of the experimental curve of interband optical conductivity. It should be mentioned that since we did not take into account matrix elements of interband transitions and the lifetime of the excited states in the calculation, such comparison has a qualitative character and there is no complete correlation in details of a fine structure of calculated and experimental curves $\sigma(E)$. Particularly, the width of maxima and ratio of their intensities in these dependences differ substantially. In addition, values of $\sigma_{theor}(E)$ at low frequencies are somewhat overestimated compared with the experiment in the context of this calculation.

For the low-energy (the Drude) spectral region, where the interband absorption minimally affects the dielectric functions, parameters that determine the dispersion of optical conductivity are associated with microcharacteristics of charge carriers. We determined plasma ω_p and relaxation γ frequencies of conduction electrons in this wavelength range (10–16 μm) using the Drude relations. The numerical values of these parameters as well as the static electrical resistance $\rho_{293\,K}$ for all compounds are presented in the table. It is known [20] that the quadrate of plasma frequency ω_p^2 in a single-electron approximation with arbitrary dispersion law $E(\mathbf{k})$ is proportional to the density of electronic states at the Fermi level. The variation in ω_p^2 with an increase in x for the family of $GdCu_x$ alloys is rather weak, although a certain increase in this parameter is observed. This tendency in general correlates with the results of calculations of the band structure of compounds under study (Fig. 1), where the found values of densities of electronic states at the Fermi level are close by magnitude. The measurements of the low-temperature heat capacity of alloys under study also show an increase in the density of electronic states near E_F with increasing the copper concentration [4]. Relaxation frequency γ additively takes into account all types of electron scattering under their excitation with the electromagnetic wave. The highest value of this parameter is found for the $GdCu_2$ compound, which corresponds to the fact that its resistivity also exceeds corresponding values of $\rho_{293\,K}$ for other compounds under study.

4. CONCLUSIONS

The electronic structure and optical properties of GdCu, $GdCu_2$, and $GdCu_5$ intermetallic compounds are investigated. Based on LSDA + U calculations of the band structure, the interpretation of frequency dependences of the interband optical conductivity of these alloys is suggested. Qualitatively, the character of the dispersion $\sigma_{ib}(E)$ is explained in terms of the calculation of the density of electronic states. It is shown that the main features of the interband absorption spectra of compounds under study are caused by quantum electron transitions between d and p bands of Cu in both spin systems as well as between d and f bands of Gd in the spin-down band system. The plasma and relaxation frequencies of conduction electrons are determined by the optical data.

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research (project no. 10-02-00546a), the MK-3376.2011.2 project, and the Analytical Departmental Target Program "Development of the Scientific Potential of the Higher School."

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Translated by N. Korovin